Synthesis of a Pyrido[1,2-*a*]benzimidazole and of an Amidine by Electrochemical Oxidation of 2,4,6-Tri-t-butylaniline in the Presence of Pyridine

By J. J. BASSELIER

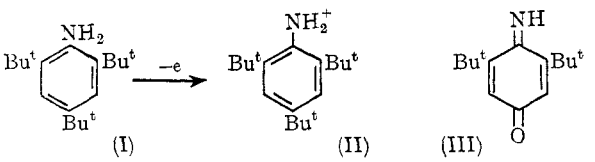
(*Laboratoire de Chimie Organique de l'Ecole Supérieure de Physique et de Chimie de Paris, 10 Rue Vauquelin, Paris, 5ème*)

and G. CAUQUIS* and J. L. CROS

(*Laboratoire d'Electrochimie Organique et Analytique du Centre d'Etudes Nucléaires de Grenoble, Cédex 85, 38—Grenoble, France*)

Summary Electrochemical oxidation of 2,4,6-tri-t-butylaniline in acetonitrile in the presence of pyridine yields 6,8-di-t-butylpyrido[1,2-*a*]benzimidazole(IVa) and the amidine (V).

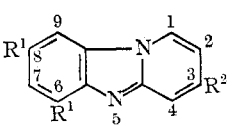
WE showed[1] that the first step in the electrochemical oxidation of 2,4,6-tri-t-butylaniline (I) in acetonitrile was the formation of the radical cation (II). We also showed that the follow-up reactions, when they are governed by the presence of a nucleophile such as water, produce the quinone-imine (III).



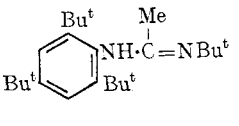
(I) (II) (III)

We now report the results obtained from electrolyses carried out in acetonitrile with 10^{-1}M-lithium perchlorate as supporting electrolyte in the presence of pyridine and some of its derivatives.

The oxidation at a controlled potential of +0·55 V *versus* the Ag/Ag^+ 10^{-2}M reference system of a 5×10^{-2}M-solution of amine (I) in acetonitrile with a tenfold excess of pyridine gives, with an apparent 2·6 electron transfer per mole of amine, two new compounds: 6,8-di-t-butylpyrido[1,2-*a*]-benzimidazole (IVa), $C_{19}H_{24}N_2$, m.p. 152—153°, and amidine (V), $C_{24}H_{42}N_2$, m.p. 160—161°, (60 and 25% yield, respectively).



(IV) a; R^1=Bu^t, R^2=H
b; R^1=R^2=H
c; R^1=Bu^t, R^2=Me
d; R^1=Bu^t, R^2=Et



(V)

In addition to elemental analyses and molecular weights measured by mass spectrometry, various spectroscopic data strongly support the structures (IVa) and (V).

Thus, the n.m.r. spectrum of compound (IVa) (100 MHz in $CDCl_3$, with $SiMe_4$ as internal lock) exhibits the eighteen protons of the two t-butyl groups at δ 1·42 and 1·67 p.p.m., the two weakly coupled benzene-ring protons at δ 7·49 and 7·67 p.p.m. (J_{79} 2 Hz.) and a complex system of four pyridine-ring protons, coupled two by two, which can be

analysed in the first order by means of double irradiation. From this analysis, the following assignments result:[2] δ_1 8·38, δ_2 6·66, δ_3 7·25, δ_4 7·68 p.p.m., and J_{12} 6·5, J_{13} 1·5, J_{14} 1·0, J_{23} 6·5, J_{24} 1·5, and J_{34} 9·5 Hz. Furthermore, the u.v. and visible absorption spectrum [cyclohexane, λ_{max} nm (log ϵ)] which shows eleven maxima, 248(4·64), 255(4·78), 265 (4·34), 274(4·26), 296(3·56), 308(3·70), 320(3·74), 344(3·60), 358(3·68), 375(3·64), and 396(3·37) is very similar to that published[3] for the pyrido[1,2-*a*]benzimidazole (IVb) itself.

Compound (V), which is formed with the participation of a solvent molecule, shows in the i.r. region the bands[4] ν_{NH} at 3450 and $\nu_{C=N}$ at 1640 cm.$^{-1}$. Besides the twenty-seven protons of the t-butyl groups attached to the aromatic nucleus (9 protons at 1·28 p.p.m. and 18 protons at 1·32 p.p.m.) and the protons of the t-butyl group of the side-chain (δ 1·48 p.p.m.), the n.m.r. spectrum exhibits two aromatic protons at δ 7·17 p.p.m. and a methyl group with an unusual shielding (δ 1·18 p.p.m.). Except for this last anomaly, all the spectroscopic data appear to be consistent with the structure (V). The anomaly could be accounted for by considering the steric influence of the two *ortho*-t-butyl groups. This produces, as shown by molecular models, a twisting of the amidine chain, submitting the methyl group to shielding by the benzene ring and by these t-butyl groups and preventing conjugation between the aromatic nucleus and the side-chain.† Such an assumption could explain also why the maxima, 210 (4·57) and 242 (4·09) in ethanol, in the u.v. absorption spectrum are observed at shorter wavelengths than in the amine (I). Unsuccessful attempts to hydrolyse this amidine are ascribed to the same steric hindrance effect.[5]

The oxidation of 2,4,6-tri-t-butylaniline in the presence of 4-picoline proceeds in an analogous fashion, yielding 3-methyl-6,8-di-t-butylpyrido[1,2-*a*]benzimidazole (IVc) (70%), $C_{20}H_{26}N_2$, m.p. 167—168° and the amidine (V) (11%). Compound (IVc) has an n.m.r. spectrum which confirms the analysis suggested for that of (IVa) (δ_1 8·35, δ_2 6·54, δ_4 7·38 p.p.m., and J_{12} 7·0, J_{24} 1·5, J_{14} *ca.* 0·0 Hz.) An additional coupling exists between the protons of the methyl group (δ 2·34 p.p.m.) and the proton at the 4-position ($J_{3-Me,4}$ 1·0 Hz.).‡

Similarly, one oxidation performed in the presence of 4-ethylpyridine gives the amidine (V) (10%) and the 3-ethyl-6,8-di-t-butylpyrido[1,2-*a*]benzimidazole (IVd) (60%), $C_{21}H_{28}N_2$, m.p. 127—128°; its n.m.r. spectrum can be analysed in the same manner.

Very different results are obtained during electrolyses carried out in the presence of 2-picoline or 2,6-lutidine. In these cases, apart from unoxidized amine and resinous products, only small quantities of quinone-imine (III) (18 and 9%), amidine (V) (13 and 5·5%) and 2,2′,4,4′,6,6′-hexa-t-butylazobenzene[1] (1·5 and 8%) have been isolated.

The details of the reaction process leading to the compounds (IVa) [or (IVc) or (IVd)] and (V) will be discussed elsewhere.[6]

We thank the Centre d'Etudes et de Recherches des Charbonnages de France for financial support.

(*Received, July 25th*, 1969; *Com.* 1126.)

† This assumption is still correct if one considers the tautomeric form of structure (V).
‡ A similar coupling, concerning a proton adjacent to a methyl group, is found in ref. 2 for the 7-methylimidazo[1,2-*a*]pyridine.

[1] G. Cauquis, G. Fauvelot, and J. Rigaudy, *Bull. Soc. chim. France*, 1968, 4928.
[2] Moreover, the work of W. W. Paudler and H. L. Blewitt (*Tetrahedron*, 1965, **21**, 353) on the n.m.r. of imidazo[1,2-*a*]pyridines supports these assignments.
[3] S. Kajihara, *J. Chem. Soc. Japan*, 1965, **86**, 839 (*Chem. Abs.*, 1966, **65**, 16935g).
[4] K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, 1962.
[5] In any case, the ease of amidine hydrolysis strongly depends upon the nature of substituents. See, for this question, R. L. Shriner and F. W. Neumann, *Chem. Rev.*, 1944, **35**, 351.
[6] G. Cauquis and J. L. Cros, to be published.